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Kinetics and mechanism of the oxidation of formic and oxalic acids by benzyltrimethylammonium tribromide

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The oxidation of formic and oxalic acids by benzyltrimethylammonium tribromide (BTMAB) leads to the formation of carbon dioxide. The reaction is first order with respect to BTMAB. Michaelis-Menten type kinetics are observed with respect to substrate. The values of the formation constants for the organic acid-BTMAB complexes and the rates of their decomposition, at different temperatures, have been determined. Oxidation of α-deuterioformic acid indicated the presence of a parimary kinetic isotope effect (k_H/k_D = 6.03 at 298 K). With an increase in the polarity of solvent, the formation constants for the complexes decrease however, their rates of decomposition increase. Suitable mechanisms involving the formation of acyclic and cyclic intermediates in the oxidations of formic and oxalic acids respectively, have been proposed.

Benzyltrimethylammonium polyhalides are widely used as halogenating and oxidizing agents in the synthetic organic chemistry[1-4]. However, not many reports seem to be available in the literature on the kinetic and mechanistic aspects of their oxidation reactions. In continuation of our earlier work on the oxidation kinetics of the primary aliphatic alcohols[5], α-hydroxy acids[6] and organic sulfides[7] by benzyltrimethylammonium tribromide (BTMAB), we report herein the kinetics and mechanism of the oxidation of formic acid (FA) and oxalic acid (OA) by BTMAB in aqueous acetic acid solution.

Materials and Methods

The organic acids available were commercial products of the highest purity and were used as such. α-Deuterioformic acid (DCOOH or DFA) was prepared by the reported methods[8]; its isotopic purity, ascertained by NMR spectra, was 94±5%. BTMAB was prepared by the reported method[1] and its purity was checked by an iodometric method. Hypobromous acid was prepared by mixing yellow mercuric oxide with bromine water, decanting and distilling *in vacuo*[9]. Acetic acid was refluxed with chromic oxide and acetic anhydride for 3 hr and then fractionated.

Stoichiometry

The oxidation of formic and oxalic acids leads to the formation of carbon dioxide. No quantitative determination of carbon dioxide formed was carried out.

To determine the stoichiometry, excess of BTMAB (× 5 or greater) was reacted with the organic acid in 1:1 (v/v) acetic acid-water mixture, and the amount of residual BTMAB after the completion of reaction was measured spectrophotometrically at 354 nm. The results indicated 1:1 stoichiometry.

Kinetic measurements

Reactions were studied under pseudo-first-order conditions by maintaining a large excess of organic acid (× 15 or more) over BTMAB. The solvent used was 1:1 (v/v) acetic acid-water mixture. The procedure for monitoring the reactions and evaluation of k_{obs} have been described earlier[5].

Spectral studies

UV-VIS spectra of (A) BTMAB (0.001 mol dm^{-3}) alone and (B) of oxalic acid (0.01 mol dm^{-3}) and BTMAB (0.001 mol dm^{-3}) were recorded on a HP diode-array spectrophotometer (Model 8452A) with a scanning speed of 600 nm s^{-1}. The solvent used was 1:1 (v/v) acetic acid-water and the temperature maintained was 279±1 K. For (A) the blank was the solvent; for (B) the blank was a solution of oxalic acid (0.01 mol dm^{-3}) in aqueous

acetic acid. The time gap between the preparation of the reaction mixture and recording of spectrum (B) was < 10 s.

Results and Discussion

The stoichiometric determination indicated the following overall reactions (Eqs 1 and 2).

$$HCOOH + PhCH_2Me_3N^+Br_3^- \rightarrow CO_2 + PhCH_2Me_3N^+Br^- + 2\,HBr \quad \ldots (1)$$

$$(COOH)_2 + PhCH_2Me_3N^+Br_3^- \rightarrow 2CO_2 + PhCH_2Me_3N^+Br^- + 2\,HBr \quad \ldots (2)$$

The reactions were found to be first order with respect to BTMAB (Table I). The rate increases with an increase in the concentration of the organic acids but not linearly (Table I). A plot of 1/[organic acid] against $1/k_{obs}$ is linear with an intercept on the rate ordinate. Thus, the reaction exhibited Michaelis-Menten type kinetics with respect to the organic acids. This indicates the following overall mechanism (Eqs 3 and 4) and rate law (Eq. 5).

$$\text{Organic Acid} + \text{BTMAB} \overset{K}{\rightleftharpoons} \text{Complex} \quad \ldots (3)$$

$$[\text{Complex}] \xrightarrow{k_2} \text{Products} \quad \ldots (4)$$

$$-d[\text{BTMAB}]/dt = \frac{k_2 K\,[\text{Organic Acid}][\text{BTMAB}]}{1 + K\,[\text{Organic Acid}]} \quad \ldots (5)$$

The dependence of the reaction rate on the acid concentration was determined at different temperatures and the values of K and k_2 were evaluated from the double reciprocal plots. Thermodynamic parameters for the complex formation and activation parameters for the decomposition of the complexes were calculated from the respective values of K and k_2 at different temperatures, respectively (Tables II and III).

Table I—Rate constants for the oxidation of formic and oxalic acids by BTMAB at 298 K in 1:1 (v/v) acetic acid-water

10^3 [BTMAB] (mol dm^{-3})	[Acid] (mol dm^{-3})	$10^3 k_{obs}$ (s^{-1})	
		Formic acid	Oxalic acid
1.0	0.02	1.82	0.67
1.0	0.03	2.61	0.93
1.0	0.04	3.29	1.14
1.0	0.06	4.73	1.53
1.0	0.10	6.61	1.92
1.0	0.15	8.80	2.40
1.0	0.20	10.0	2.68
1.0	0.10	6.65*	1.88*
2.0	0.10	6.70	1.90
3.0	0.10	6.64	1.93
4.0	0.10	6.55	1.98
8.0	0.10	6.69	1.89

*contained 0.005 mol dm^{-3} acrylonitrile

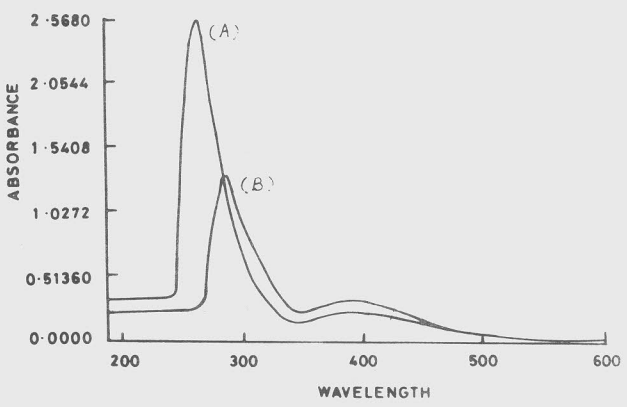


Figure 1—UV-VIS spectra of (A) BTMAB (0.001 mol dm^{-3}) and (B) BTMAB (0.001 mol dm^{-3}) + oxalic acid (0.01 mol dm^{-3})

The formation of an intermediate complex was also confirmed from spectral studies. A perusal of spectra, (A) and (B) showed a clear difference in the two spectra (Figure 1). Addition of oxalic acid causes the disappearance of the peak at 264 nm and a new peak of small height appears at 286 nm. The height of the new peak decreases with time. Also there is distinct increase in the absorbance of BTMAB at 392 nm on addition of oxalic acid. This supports the postulation of the formation of an intermediate complex in the pre-equilibrium.

The oxidation of α-deuterioformic acid (DFA) showed that the formation constants of the complexes of ordinary and deuteriated formic acids have similar values (Tables II and III), however, the rate of decomposition of the complexes exhibited a substantial primary kinetic isotope effect ($k_2(H)/k_2(D)$ = 6.03 at 298 K). The rate of oxidation of the deuteriated acid was corrected for the ordinary acid present.

To study the effect of solvent composition on the oxidation, the dependence on reductant concentration was studied in solvents of different compositions. Results showed that the formation constant, K, decreases while the rate constant (k_2) for the decomposition of the complex, increases with an increase in the water content of the solvent mixture (Table IV).

Table II—Formation constants and thermodynamic parameters of the organic acid-BTMAB complexes in 1:1 (v/v) acetic acid-water

Acid	Formation constant (dm^3 mol^{-1}) at				ΔH	ΔS	ΔG
	293 K	298 K	313 K	318 K	(kJ mol^{-1})	(J mol^{-1} K^{-1})	(kJ mol^{-1})
FA	6.05	4.87	3.93	3.22	–34.1±0.2	–93±1	–6.42±0.2
OA	19.9	10.3	5.65	3.01	–96.5±0.8	–296±3	–8.30±0.6
DFA	6.15	4.80	3.91	3.30	–33.6±1.0	–92±3	–6.43±0.8

Table III—Rate of decomposition and activation parameters of the organic acid-BTMAB complexes in acetic acid-water (1:1; v/v)

Acid	10^2 k_2 s^{-1} at				ΔH^*	ΔS^*	ΔG^*
	293 K	298 K	303 K	308 K	(kJ mol^{-1})	(J mol^{-1} K^{-1})	(kJ mol^{-1})
FA	1.52	2.05	3.11	4.14	48.8±1.8	–114±6	82.6±1.4
OA	2.98	3.93	5.00	6.55	36.6±0.5	–150±2	81.1±0.4
DFA	0.25	0.34	0.52	0.68	48.9±2.0	–128±6	87.0±1.6

Table IV—Dependence of k_{obs} on the concentrations of the acids in solvents of different compositions {[BTMAB] = 0.001 mol dm^{-3}, Temp. = 298 K}

[Acids] (mol dm^{-3})	10^3 k_{obs} s^{-1} [at % AcOH (v/v)]											
	20		30		40		50		60		70	
	FA	OA	FA	OA	FA	OA	FA	OA	FA	OA	FA	OA
0.02	3.58	11.1	2.84	9.31	2.33	8.45	1.82	6.70	0.99	3.71	0.75	2.97
0.03	5.26	16.5	4.16	13.5	3.45	12.1	2.61	9.30	1.42	5.10	1.02	3.78
0.04	6.93	21.0	5.43	17.0	4.38	15.1	3.29	11.4	1.80	6.02	1.24	4.50
0.06	9.89	29.7	7.68	23.5	6.30	20.3	4.73	15.3	2.38	7.54	1.69	5.46
0.10	15.5	43.8	12.0	33.4	9.25	28.4	6.61	19.2	3.28	9.48	2.18	6.61
0.15	21.0	58.3	15.5	43.5	12.3	34.4	8.80	24.0	4.11	10.4	2.65	7.28
0.20	26.3	69.2	19.3	50.3	14.6	39.7	10.0	26.8	4.66	11.6	2.91	7.78
					K (dm^3 mol^{-1})							
	2.12	3.54	2.77	5.28	3.45	7.22	4.87	10.3	7.15	16.5	10.6	22.7
					10^2 k_2 s^{-1}							
	8.82	16.9	5.43	9.79	3.64	6.73	2.05	3.93	0.80	1.51	0.43	0.95

Table V—Effect of addition of benzyltrimethylammonium chloride (BTMACl) on the rate of oxidation {[BTMAB]=0.001 mol dm^{-3}, [Acid]=0.10 mol dm^{-3}, Temp.=298 K}

10^3[BTMACl]	$10^3 k_{obs}$ s^{-1}	
mol dm^{-3}	FA	OA
1.0	6.61	1.92
2.0	6.72	1.98
3.0	6.57	1.85
6.0	6.60	1.90
8.0	6.48	1.99

Table VI—Effect of addition of sodium bromide on the rate of oxidation {[BTMAB] = 0.001 mol dm^{-3}, [Acid] = 0.10 mol dm^{-3}, Temp. = 298 K}

10^3 [Br^-]	$10^3 k_{obs}$ s^{-1}	
mol dm^{-3}	FA	OA
1.0	6.61	1.92
2.0	6.52	1.83
3.0	6.80	1.94
6.0	6.60	1.99
8.0	6.63	1.89

Addition of benzyltrimethylammonium chloride or bromide ion had no effect on the rate of oxidation (Tables V and VI).

The oxidation of organic acids, under a nitrogen atmosphere, failed to induce the polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the reaction rate (Table I). Thus, a one-electron oxidation, giving rise to free radicals, is unlikely.

Oxidation by bromine

The rate of oxidation of formic acid by bromine, under similar conditions, was more than double than the oxidation by BTMAB. The reaction showed first order dependence on [formic acid]. The rate of oxidation by bromine is retarded by the addition of bromide ion (Table VII).

Conductivity measurements have shown[6] that BTMAB is an ionic compound which exists under our reaction conditions as benzyltrimethylammonium and tribromide ions (Eq. 6). No effect

of added benzyltrimethylammonium ion (Table V) also indicates that the following equilibrium (Eq. 6) lies far towards right.

$$PhCH_2Me_3NBr_3 \rightleftharpoons PhCH_2Me_3N^+ + Br_3^- \quad \ldots (6)$$

The other equilibria which may exist in the solution are as shown in Eqs 7 and 8.

$$Br_3^- \rightleftharpoons Br_2 + Br^- \quad \ldots (7)$$

$$Br_2 + H_2O \rightleftharpoons HOBr + HBr \quad \ldots (8)$$

Table VII—Rate constants for the oxidation of formic acid by bromine at 298 K in 1:1 (v/v) acetic acid-water solution

[FA] mol dm^{-3}	10^3[Bromine] mol dm^{-3}	$10^4 k_{obs}$ s^{-1}
0.02	1.0	9.78
0.04	1.0	19.3
0.06	1.0	30.3
0.10	1.0	50.0
0.20	1.0	105
0.10	2.0	51.1
0.10	5.0	53.1
0.10	10.0	49.9
0.10	1.0	32.2[a]
0.10	1.0	11.5[b]
0.10	1.0	8.90[c]

(a), (b) and (c) contained 0.001, 0.005 and 0.01 mol dm^{-3} sodium bromide respectively

The probable oxidizing species in a solution of BTMAB are, therefore, tribromide ion, molecular bromine or hypobromous acid. The concentrations of bromine and hypobromous acid will be very small as dissociation constant of tribromide ion is very low[10]. Further, the dissociation is likely to be suppressed by the addition of bromide ion. There was no effect of added bromide ion on the reaction rate. Therefore, it is unlikely that Br_2 or HOBr play any role in the oxidation process. The postulation is supported by the different kinetic pictures exhibited by the oxidation of formic acid by BTMAB and bromine.

In the oxidation of formic acid by HOBr the curve of log [oxidant] against time, started very flat and became steeper as the reaction proceeded. This could be attributed to the reduction of HOBr to bromide ion which reacted with unchanged HOBr to give bromine which oxidised formic acid rapidly. This type of kinetic feature was not observed in the present reaction system. Thus, HOBr is not likely to be a reactive oxidizing species here. Therefore, the most likely reactive oxidizing species, in this reaction, is tribromide ion.

The decrease in the magnitude of K, with an increase in the polarity of the medium, may be attributed to the fact that when an anion reacts with a neutral molecule to form a complex, the charge will be dispersed over a somewhat larger area in the transition state. Thus, the charge density will diminish and the complex formation will be facilitated by a decrease in the water content of the solvent mixture[11]. This is in accord with the suggestion that the active oxidizing species is tribromide ion.

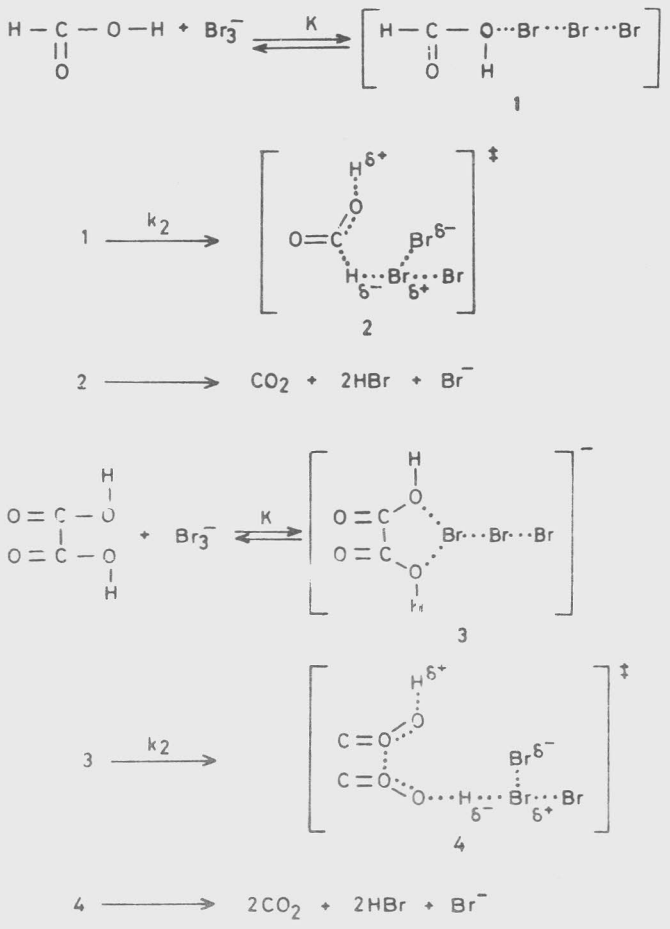
The solvent effect was analysed using the Grunwald-Winstein[12] equation.

$$\log k_2 = mY + \log k_0 \quad \ldots(9)$$

The plots of log k_2 against Y. for both formic and oxalic acids, are linear (r = 0.9994 and 0.9997) with m = 0.66±0.01 and 0.63±0.01 respectively. The positive values of m point to a transition state which is more polar than the reactant. Thus, it seems that considerable charge separation takes place in the transition state for the decomposition of the complex.

Mechanism

The rate law (Eq. 5), indicates that an intermediate complex is formed in a rapid pre-equilibrium. The formation of an intermediate complex is supported by the spectral studies also. A complex may be formed by the interaction of non-bonded pairs of electrons of the carboxylic-oxygens and BTMAB, as suggested in our earlier reports[5,6]. Thermodynamic parameters indicate that the BTMAB-OA complex is more stable than the BTMAB-FA complex. The substantial kinetic isotope effect in the oxidation of formic acid confirms the cleavage of the α-C-H bond in the rate-determining step. The temperature invariance of the primary kinetic isotope effect (*cf.* Table III) can be interpreted in terms of a mechanism in which two bonds are cleaved more or less synchronously. Therefore, a rate-determining step involving cleavage of C-H and O-H bonds can be envisaged. The oxidation of the oxalic acid, however, involves a rate-determining C-C bond cleavage. In the oxidation of oxalic acid, the formation of a cyclic anhydride intermediate is a distinct possibility, though there is no compelling evidence for it. The relatively large magnitude of the unfavourable entropy for the formation of the intermediate complex, supports the formation of a more ordered complex in the oxidation of oxalic



Scheme I

acid. The formation of a cyclic anhydride as an intermediate was also postulated in the oxidation of oxalic acid by chromic acid[13] and pyridinium hydrobromide perbromide[14]. The mechanism shown in Scheme I accounts for all the observed data.

It is of interest to compare the results obtained in the present reaction with those obtained in the oxidation of α-hydroxy acids[6]. The kinetics are similar and the reactive oxidizing species in both the cases is tribromide ion. The major difference is the absence of a kinetic isotope effect in the oxidation of mandelic acid. The rate-determining step, in that case, did not involve a cleavage of the α-C-H bond. The intermediate complex collapses to an acyl hypobromite derivative.

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References

1 Kajigaeshi S, Kakinami T, Tokiyama H, Hirakawa T & Okamota T, *Bull Chem Soc Jpn,* 60, **1987**, 2667.
2 Kajigaeshi S, Moriuaii M, Tanaka T, Fujisaki S, Kakinami T & Okamoto T, *J Chem Soc, Perkin Trans,* 1, **1990**, 897.
3 Kajigaeshi S, Shinmasu Y, Fujisaki S & Kakinami T, *Bull Chem Soc Jpn,* 63, **1990**, 941.
4 Kajigaeshi S, Murakawa K, Fujisaki S & Kakinami T, *Bull Chem Soc Jpn,* 62, **1989,** 3376; Kajigaeshi S, Kawamukai H & Fujisaki S, *Bull Chem Soc Jpn,* 62, **1989**, 2585.
5 Goel S, Kothari S & Banerji K K, *J Chem Res,* **1996** (*S*), 230; (*M*) 1318.
6 Goel S, Kothari S & Banerji K K, *Indian J Chem,* 35B, **1996**, 1180.
7 Goel S, Kothari S & Banerji K K, *J Chem Res,* **1996** (*S*), 510; (*M*) 2901.
8 Wiberg K B & Stewart R, *J Am Chem Soc,* 78, **1956**, 1214.
9 Knoller Y & Pearlmutter-Hayman B, *J Am Chem Soc,*, 77, **1955,** 3212.
10 Jones G & Backstorm S, *J Am Chem Soc,* 56, **1934**, 1517.
11 Gould E S, in *Mechanism and Structure in Organic Chemistry,* (Holt, Rinehart and Winston, Inc New York), **1964**.
12 Falnberg A H & Winstein S, *J Am Chem Soc,* 78, **1956**, 2770.
13 Hassan F & Rocek J, *J Am Chem Soc,* 94, **1972**, 9073.
14 Suri D, Banerji K K & Kothari S, *J Chem Res,*; 1996 (*S*), 228; (*M*), 1301.